Overview

To provide an accurate description of the fate of metal contaminants, such as Ni, in heterogeneous systems, such as aerial-contaminated soils neighboring a smelter refinery, it is essential to understand its speciation. Macroscopic chemical analyses are not sufficient and hence they must be complemented with advanced molecular scale techniques to obtain a detailed picture of such complicated systems. This research demonstrates the need to combine bulk and micro-focused X-ray absorption spectroscopic (XAS) techniques to identify Ni species, on the molecular scale, in surface soil samples collected from an area around this refinery.

The micro-focused studies were conducted at ALS 10.3.2 (Lawrence Berkeley Laboratory, CA) and X26A (NSLS, Brookhaven National Laboratory, NY), while the bulk spectroscopic studies were conducted at beamline X11A (NSLS, Brookhaven National Laboratory, NY). The XAS data were collected, *in situ* on the samples, at Ni K-edge and analyzed using WinXAS (Version 2.1). Combined results of these spectroscopic studies reveal that Ni in the soils located closer to the refinery, (pH 5.9-6.6), is dominantly in the form of nickel oxide. On the other hand, in the soil samples (~ pH 7) collected at least 3.0 km from the refinery, nickel predominantly exists as a disordered hydroxide species. Interestingly, soil samples that were collected from intermediate locations, contained significant fractions of both nickel oxide and the disordered hydroxide species. Micro-XRF analyses reveal that these Ni species are discrete spherical to elliptical particles that are neither associated with any of the mineral phases in the soils nor co-precipitated with other metals. Nickel does not appear to be associated with Fe or Mn components of the soils. Inclusion of Ni-Fe and/or Ni-Mn contributions in fitting the second shells of the Fourier transforms of the soil samples result in invalid fits. Similarly, the second shell features, as noted from the bulk and micro-XAS analyses, do not provide sufficient evidence to assume that a significant fraction of Ni species may have reacted with Al-bearing clays and clay minerals to form LDH-like structures. Ni species do not appear to be associated with the organic fractions of the soils. Although the associations of Ni with any of the soil components are not evident in the current studies they must not be completely ruled out since it is likely that the signals from the high concentrations of NiO species may swamp the signals arising from the sorption complexes. Both the bulk XAS analyses and the micro-XAS analyses confirmed that Ni predominantly exists as oxide or hydroxide species. As a result, linear combination analyses were constrained to estimating the relative concentrations of NiO and $Ni(OH)_2$ in the soil samples, where the Ni-Ni bond distance and coordination number in the second shell are the key parameters for distinguishing between these species. Consistently, the linear combination analyses suggest that in the soil samples closest to the smelter refinery, approximately 90-95% of the Ni species present exists as NiO. On the other hand, $Ni(OH)_2$ comprises nearly 92-97% of the Ni in the farthest soil samples. In addition, the intermediate soil samples contained approximately 30-35% NiO. The above results invoke the need to conduct fundamental studies probing the physicochemical processes governing the short- and long-term mobility and bioavailability of nickel in the presence of various dissolution agents that are present in most soil and aquatic environments.

Material and Methods

Soil Samples Studied

Soil Sample	pH
TP3	6.59
GROETLAER	5.87
SS11	6.75
HRUSKA	6.49
HSTONE	7.17
SS18	6.90

Bulk XAS

In situ XAS data were acquired on

• Beamline X11A at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, Upton, NY.

• At Ni K-edge over the energy range 8183-9082 eV in fluorescence mode using a Ge solid-state multi-element detector.

•Ni reference standards were studied in transmission mode.

SXRF and m-XAS

Spatially resolved µ-XAS and µ-SXRF data were collected

• At ALS 10.3.2 at Lawrence Berkeley National Lab and X26A at NSLS, Brookhaven National Laboratory.

•At the Sr K-edge to identify metals including: Ni, Fe, Co, Cu, Zn, and Mn.

•Using a Si solid-state multi-element detector

•Mapping regions ranged from 400×400 to 1000 ×1000 μm^2.

• Step size of 5 µm and an integration time of 100 ms.

•µ-XAS spectra were collected on the regions indicative of significant Ni concentrations at Ni K-edge.

•*Data Analyses* performed using WinXAS (version 2.1).